ELECTROGRAPHIC EXAMINATIONS OF PULVERIZED ORE SAMPLES AND ORE CONCENTRATES

PRELIMINARY REPORT

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INTRODUCTION

For the qualitative chemical analysis of metals, alloys and conducting ore minerals (polished ore sections), for simple electro spot testing, furthermore for the examination of the distribution of inclusions, as well as for examination of the macrostructure electrography has proved to be very suitable, this procedure has been applied since a relatively long time.

The most important advantages of the method are: a) the composition of the sample may be quickly and simply established without injury of its surface; b) at the detection of the single metals — using suitable selective and sensitive, mainly organic reagents — the separations which are indispensable for customary chemical qualitative analyses can be avoided; c) small amounts of the samples are also sufficient for the examinations and small amounts of metal can be precisely detected too.

Hitherto, electrographic examinations only involved the qualitative chemical, or textural analysis of metal-, alloy- or ore samples. Concerning the type of examinations mentioned above numerous valuable data and establishments may be found in the works of *Fritz, Glazunov, Niessner, Jirkovsky; Hiller, Yagoda* as well as in those of *Hermance* and *Wadlow*, only to enumerate the fundamental and detailed works.

Some works *(Hiller, Štemprok,* Туровский) refer to the electrographic identification of single granules, inclusions observed in polished ore sections or to that of free ore fragments and individual granules, respectively, through the detection of the metals obtained in them, however, the electrographic examination of pulverized ore samples, or ore concentrates has so far not been attempted. The advantages of the electrography outlined above, however, suggest the expediency of trying to apply the method for pulverized ore samples, as well as for the qualitative chemical analysis of ore concentrates.

In the case of single ore granules the examination is very simple: the granule is placed onto a reagent paper lying on an aluminum plate which is connected to the negative pole of a battery, then the granule is brought

into contact with a platinum wire connected to the positive pole of the battery. After about 20—30 seconds it can be established whether or not the anticipated reaction — showing the presence of the metal sought for — has taken place on the corresponding reagent paper. According to the size of the granule the examination may also be carried out under the microscope.

The tasks at the examination of pulverized ore samples can be outlined as follows:

1. In which way the customary electrographic procedure should be modified for the qualitative examination preceding the chemical quantitative analysis of ore samples and for the establishment of the composition and impurities of ore concentrates, respectively.

2. The minimum amount of the single metals wich under given experimental conditions can still be detected precisely by the electrographic examination of pulverized ore samples must be established, furthermore, it must be examined how the different ores and metals, respectively, contained in pulverized mixtures interfere with the detection of one another.

3. Finally, it must also be verified in some way if the procedure cannot also be applied for examinations of semiquantitative character.

EXPERIMENTAL

For the examination of ore powders, of course, the same principle holds good as that generally valid for electrographic examinations, only a solution for the carrying out of the procedure must be found.

The first task is therefore the development of the most appropriate standard method of examination which warrants that for examinations in series too the experimental conditions are identical. This problem involves the preparation of the sample to be examined as well as the construction of a suitable mounting block.

For the preparation of the sample and the carrying out of experiments — bearing in mind the possible need for a comparison of the single examinations in series and the different prints, respectively — the following must be taken into account:

a) the size of the surface on which the samples come into contact with the reagent paper must be identical

b) the examinations must be carried out under identical pressure

c) the ore powder must not adhere to the surface of the gelatine paper

d) it must be possible to make simultaneously — under completely identical experimental conditions (electrolyte, pressure, voltage, time) — prints of several samples, but it must also be feasible to examine the single samples separately.

For the preparation of the samples the following procedure seemed suitable: the ore powder is mixed with plaster of Paris and by adding a little water a pulp is prepared of this mixture, which is pressed into a suitable form till binding. A mixture in which the ratio of the ore powder: plaster of Paris was 2 : 1, bound well, its firmness was adequate, the conducting was also established through the ore granules in the plaster matrix

being in contact with one another, however, the print developed slowly and with poor intensity. In addition, if the preparation of the samples for examinations in series were carried out in this way just one of the advantages of the method of the electrography — the rapidness — would be eliminated. Another solution would be to press the ore powder into pastils and then to print. If the powder is very fine it may be pressed into pastils. However, if the fractions are coarser it can no more be accomplished, but even if the pastils are prepared of fine fractions they may also deteriorate when they are pressed onto the reagent paper.

Finally, the following solution seems to be appropriate in all cases: the mounting block is made of plexy-glass the size of its surface is 7×9 cm and the height 2 cm, the samples are inserted into 12 bores penetrating entirely through the block. The diameter of each of the bores is 9 mm. The backing sheet is placed onto the aluminum plate which serves as cathode and onto this the printing paper is laid. If a direct print should be prepared the printing paper must be impregnated with the suitable electrolyte and reagent, if on the other hand, only a latent print should be made the gelatine paper is simply only imbibed with the electrolyte of choice.

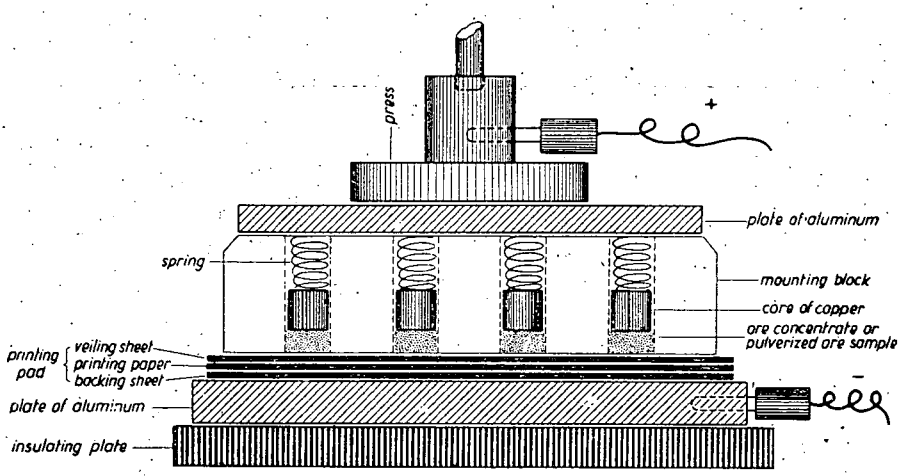


Fig. 1. The mounting block for the electrographic examination of pulverized ore samples. The arrangement of the samples, printing pad and electrodes

If the fine ore powder comes into direct contact with the gelatine paper it adheres to its surface soiling it and renders particulary in the case of faint colouration the precise identification impossible. This possible error may be avoided if — before the mounting block is put onto the surface of the gelatine paper — a thin paper (cigarette paper) moistened with the electrolyte applied is smoothed onto it and the excess moisture of the gelatine paper and of this veiling sheet smoothed onto it are simultaneously rolled with a rubber roller between two clean blotting papers. This also causes the protective layer to adhere without forming air-

bubbles to the reagent paper. Thus the samples come into direct contact with this veiling sheet which the ions can penetrate during the electrolysis easily, thus the printing time is not either prolonged, and the surface of the reagent paper remains quite clear so that the colouration on it is well visible, i. e. the latent print can also be developed without any disturbing interference.

The mounting block is placed onto the veiling sheet, the powder samples are strewn into the bore-holes and the powder is uniformly distributed and pressed by means of a glass rod, then a copper or aluminum core — the diameters of which correspond to the bore — is placed over the powder into the bore-holes and finally onto each core a spring of suitable strength is adjusted. The springs protrude about 5—6 mm out of the mounting block. The springs are pressed down by an aluminum plate and the mounting block — clamped between two aluminum plates — is inserted into the press used for electrography.

The dimension of the bore-holes may of course be chosen arbitrarily. If only simple qualitative spot testing should be accomplished using small quantities of the substance bore-holes of far smaller dimension then those mentioned above are suitable, whereas if the colour intensities of print-series should be compared, it is advisable — in order to obtain a colour spot with a larger surface — to use a mounting block provided with bore-holes of larger diameter. The above mounting block renders possible the simultaneous printing of 12 samples, of course, single samples can also be printed. If the comparison of the colour intensity of the prints is not important and the samples should be examined one by one the mounting block is not introduced into the press, but the samples are inserted into the mounting block placed on the printing pad, the copper core is put onto it and the banana plug at the end of the lead connected with the positive pole of the battery is mildly pressed to it.

According to points (a — d) described at the beginning of the Experimental the construction of the mounting block, as well as the technic outlined is very suitable, thus the tasks outlined in paragraph 1 of the Introduction concerning the electrographic examination of pulverized ore samples have been solved satisfactorily. As regards the electrographic examinations of pulverized ore samples the present paper will merely still deal with a few establishments summarised briefly in the following.

If identical samples are introduced into the bore-holes and the prints prepared simultaneously, the intensity of all the prints will be the same considering that all the experimental conditions i. e. the voltage, current, electrolyte, reagent, pressure, timing and the resistance of the single samples are quite identical. The prints demonstrated on Fig. A. of the Plate were prepared from niccolite powder on dimethylglyoxim reagent paper by simultaneous printing.

If on the other hand, different per se homogeneous ore samples are introduced into the single bore-holes and printed simultaneously on a reagent paper specific for a given metal, the colour intensity of the prints of the individual samples will not necessarily be in every case and ore the same. Thus, for instance, on introducing into the 12 bores of the mounting block 2—2 samples of covellite, enargite, tetrahedrite, chalco-

pyrite, pyrrhotite, and pyrite and using α-α'-dipyridyl reagent paper and printing them simultaneously (2,2 V, 5 mA, 2 minutes) the print density of the two prints of the same minerals was identical, but e. g. the print of pyrrhotite was fainter than that of pyrite, that of enargite fainter than that of covellite and that of tetrahedrite only just visible, as can be seen on Fig. B. of the Plate.

However, if only 1—1 sample was taken of the above ores, i. e. 6 various ore samples were printed simultaneously on the reagent paper mentioned above at 6 V, 20 mA, 1 minute, the density of the prints obtained from all the samples was well detectable, but as can be seen on Fig. C. of the Plate the intensities also varied in this case, for example those of pyrite and pyrrhotite and enargite, tetrahedrite and covellite, respectively.

The above facts may be interpreted as follows:

In the case of a given reagent the print density depends upon the quantity of the ions dissolved from the sample and fixed in the reagent paper as insoluble coloured compound. The amount of the dissolved ions is, however, among others also influenced by the current. If the boreholes contain samples of identical composition and resistance the current through the electrographic cell recorded on the milliammeter of the electrographic equipment is distributed uniformly through the single samples and considering that all other conditions are also identical the density of the prints obtained is also the same. If on the other hand, the bore-holes contain various ore samples these come through the copper core — spring — upper aluminum plate — spring — copper core into metallic contact with one another and are also in contact with the same electrolyte, hence they may form local cell systems. Similarly local cells may also be created between the different ore samples and the lower aluminum plate. It can thus be visualised that if this assembly functions as a primary cell without an external power prints are merely obtained of those ores which as compared with the others have more anodic character, whereas the more cathodic specimens would not be dissolved and hence would not be printed. If, however, a current supply is applied and the potential across the cell is sufficient to render all the specimens completely anodic, practically all elements may be forced from the surface of the samples into the printing medium and also in the case of different ore samples prints with satisfactory density will be obtained from each single sample. The two exemples mentioned above show too that if enargite and tetrahedrite are printed simultaneously with other ore samples at 2,2 V only very poor prints were obtained, whereas at 6 V in the case of the same ores the density of the prints of enargite and tetrahedrite was very suitable. Hence, it is possible to obtain prints from different samples simultaneously. Differences in intensity may also further prevail because there may further exist differences in resistance of the single samples owing to which the distribution of the current passing through will not be uniform, thus in spite of the identity of voltage, pressure and time there will still exist differences between the amounts of ions forced into the printing medium and thus also between the print densities.

If various kinds of ores are examined simultaneously and the first print shows that the intensity of some of the prints is very poor the following ones must be printed singly and care must be taken that the electrolysis is carried out identically in the case of each sample, thus the second print will already be well identificable and the density of the prints will be appropriate.

If in the ore examined different kinds of sulphide minerals are present and it must be decided whether the ore powder contains e. g. Co, Ni, Fe and Cu, the examination is simple. Gelatine paper strips provided with a veiling sheet and singly impregnated with reagents specific for the metals to be detected are placed side by side under the mounting block, the samples are strewn into the bore-holes and printed. The prints may be made simultaneously from several samples, as if the ore powder to be examined is also in itself a mixture of different minerals, the composition and behaviour of the mixture introduced into all the bore-holes is the same. Sometimes it is better to make latent prints, particularly if at the detection of the single metals it may be anticipated that interfering ions will have to be masked. Thus for instance, in the above case if Co should be detected with α-nitroso-β-naphtol and the presence of iron and copper must be taken into account, it is advisable merely to permeate the strip used for the detection with a solution of sodium phosphate + potassium iodide to mask the interfering metals mentioned, and only to develop subsequently the latent print in the reagent. On the other hand, e. g. the detection of iron or copper with α-α'-dipyridyl can in all cases be carried out directly on the paper impregnated with the reagent, as in the case of this reagent there are no interfering ions. Besides just in the case of this reagent, as well as in that of all reagents which form coloured soluble complexes with metal ions and not an insoluble precipitate, the direct printing is more suitable as if one would attempt to develop latent print in such reagents, instead of a clear, sharp print an indistinct, blurred spot would be obtained. On the other hand, in the case of reagents which form an insoluble precipitate with the metal, it is often better to prepare first a latent print and develop them subsequently, as in the case of direct printing a thin precipitate layer can form already on the surface of the anode which may easily block the further penetration of the metal ions into the reagent paper.

The elaboration of the course of the electrographic analysis of different pulverized ore samples and ore concentrates, the establishment of the smallest quantities of metal which can be still detected by electrographic examination of such samples is in progress.

REFERENCES

1. Fritz, H.: Studien über die Empfindlichkeit einiger charakteristischer chemischen Farbreaktionen mit Hilfe der Elektro-Tüpfelmethode. Z. f. anal. Chem, vol. 78. pp. 418—427. 1929.
2. Fritz, H.: Über einige neue Ausführungsformen der Elektro-Tüpfelanalyse. I. Theoretische Grundlagen. Mikrochemie, vol. 19. pp. 6—16. 1935.
3. Fritz, H.: Über einige neue Ausführungsformen der Elektro-Tüpfelanalyse. II. Die Elektro-Strichmethode. Mikrochemie, vol. 21. pp. 47—56. 1936.

4. Fritz, H.: Experimentelle Beiträge zum Ausbau der Elektro-Tüpfelanalyse. 2., 3., 4., 5. Mitteilungen. Mikrochemie, vol. 22. pp. 161—181. 1937., vol. 23. pp. 31—78. 1937. vol. 24. pp. 22—28. 1938., vol. 24. pp. 171—178. 1938.
5. Glazunov, A.: O elektrografickém způsobu reprodukce makrostruktury. Strojnický obzor, No. 24. p. 445. 1929.
6. Glazunov, A.: Nouvelle méthode d'analyse rapide des alliages sans destruction de l'échantillon. Compt. Rend. de 9-ème Congrès de Chimie Industrielle, 1930.
7. Glazunov, A.: Electrographic Method of Analysis. Metal Progress, vol. 24. 1933 (Oct).
8. Glazunov, A. and Křivohlavý, J.: Quantitative Bestimmung des Nickels in Nickelstählen auf elektrographischem Wege. Z. f. phys. Chem. A. 161. p. 373. 1932.
9. Glazunov, A. and Jeníček, L.: Die elektrographische Methode und ihre Anwendung zur Prüfung von Lacküberzügen: Korrosion und Metallschutz, vol. 16. pp. 341—344. 1940.
10. Grasselly, Gy.: Qualitative chemische Untersuchungen an sulfidischen Erzanschliffen. Acta Geologica Acad. Sci. Hung. vol. 1. Fasc. 1—4. pp. 79—94. 1952.
11. Grasselly, Gy.: Electrographical Analysis of Ore Textures. Acta Min. Petr. Univ. Szegediensis, Tom. VI. pp. 47—57. 1952.
12. Hermance, H. W.: Printing techniques in analytical chemistry. Bell Laboratories Record, Tom. 18. No. 9. p. 269. 1940.
13. Hermance, H. W. and Wadlow, H. V.: Electrography and Electro-Spot Testing. Berl: Physical Methods in Chemical Analysis. vol. II. pp. 155—228. Academic Press, New York, 1951.
14. Hiller, Th.: Sur l'application de la méthode des empreintes à la détermination des minéraux opaques en section polie. Schweiz. Min. Petr. Mitt. vol. 17. p. 88. 1937.
15. Hruska, J. H.: The Practical Application of Electro-Chemistry to Modern Macrography. Heat Treating and Forging, vol. 17. pp. 1034—1037. 1931.
16. Hunter, M. S., Churchill, I. R. and Mears, R. B.: Electrographic Methods of Surface Analysis. Metal Progress, vol. 42. pp. 1070—1076. 1942.
17. Jirkovský, R.: Elektrographische Methoden (Sammelreferat), Mikrochemie, vol. 15. pp. 331—342. 1934.
18. Niessner, M.: Neue Wege zur chemischen Identifizierung von Legierungszusätzen und Inhomogenitäten in metallischen Werkstofen. Mikrochemie, vol. 12. pp. 1—24. 1932.
19. Štemprok, M.: Použiti kapiláry při elektrografickém určovani rud. Chemické listy, ročnik 45. p. 456. 1951.
20. Štemprok, M.: Elektrographische Methode in der Erzmikroskopie unter Anwendung des Cellophans. Chemie der Erde, vol. 16. p. 232. 1953.
21. Туровский, С. Д.: Применение химических реакций по методу отпечатков при изучении шлихов и тяжелых фракций протолочек. Записки всесоюзн. мин. общ. Втор.сер. Вып. 4. Москва, 1954.
22. Yagoda, H.: Semiquantitative Tüpfelproben durch Begrenzung der Reaktionsfläche. Mikrochemie, vol. 24. pp. 117—130. 1938.
23. Yagoda, H.: Analytical Patterns in the Study of Minerals and Biological Materials. Ind. Eng. Chem. Anal. Ed. vol. 15. p. 135. 1943.

EXPLANATION OF THE PLATE

A) PRINTS OF NICCOLITE SAMPLES

Printing conditions

Electrolyte: 0,5 M Na_2SO_4 Latent simultaneous printing
Current: 10 milliamp. Voltage: 2 volts Time: 60 seconds
Latent print developed in 1% alcoholic solution of dimethylglyoxime

B) PRINTS OF VARIOUS ORE SAMPLES

1—2 covellite 7— 8 tetrahedrite
3—4 chalcopyrite 9—10 pyrrhotite
5—6 enargite 11—12 pyrite

Printing conditions

Electrolyte: 0,5 M Na_2SO_4 Direct simultaneous printing
Reagent: 0,5% aqueous solution of α-α'-dipyridyl
Current: 5 milliamp. Voltage: 2,2 volts Time: 2 minutes

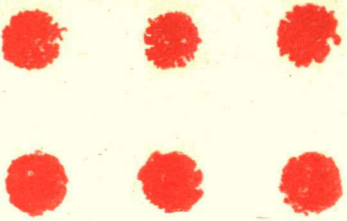
C) PRINTS OF VARIOUS ORE SAMPLES

1. tetrahedrite 2. enargite 3. covellite
4. chalcopyrite 5. pyrrhotite 6. pyrite

Printing conditions

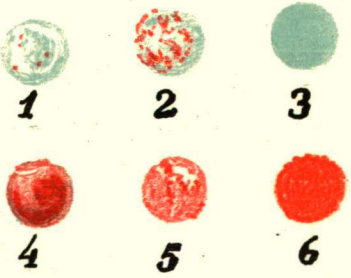
Electrolyte: 0,5 M Na_2SO_4 Direct simultaneous printing
Reagent: 0,5% aqueous solution of α-α'-dipyridyl
Current: 20 milliamp. Voltage: 6 volts. Time: 1 minute

The enclosed reproduction of the original prints reflects only approximately the discrepancies in colour intensity of the original prints. Its communication owing to the references in the text can not be neglected.



A.

B.



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